International Journal on Emerging Technologies **11**(5): 193-196(2020)

ISSN No. (Print): 0975-8364
ISSN No. (Online): 2249-3255

Synthesis and Crystal Structure of [tetrakis(μ-caprylato)-bis-(4-cyanopyridine) copper(II)]

S. Baruah[1], N. Sarmah[1] and B. K. Das[2,3]
[1]Ph.D. Student, Department of Chemistry, Gauhati University, Guwahati, India.
[2]Professor, Department of Chemistry, Gauhati University, Guwahati, India.
[3]Vice Chancellor, Bhattadev University, Pathsala, India.

(Corresponding author: S. Baruah)
(Received 20 June 2020, Revised 24 July 2020, Accepted 14 August 2020)
(Published by Research Trend, Website: www.researchtrend.net)

ABSTRACT: Copper(II) carboxylates and their complexes especially with nitrogen donor ligands have already been widely studied but copper(II) carboxylates containing long alkyl chains are rarely reported. Long chain copper complexes are more soluble in less polar organic solvents and thus it may be expected that such systems will be more effective as selective, molecular homogenous catalysts. We hereby report the synthesis of a new copper(II) caprylate or octanoate of formula $[Cu_2(\mu\text{-}O_2CC_7H_{15})_4(4\text{-}CNpy)_2]$ (4-CNpy = 4-cyanopyridine) and characterize by single crystal X-ray diffraction. From crystal structure analyses, the compound is found to be dimer with the familiar *paddle-wheel* or lantern geometry. In the structure, each copper(II) atom has distorted square pyramidal geometry and are bridged by the carboxylate anions. Substituted pyridine ligands occupy the apical positions through the pyridyl nitrogen atom.

Keywords: crystal structure; dicopper complex; caprylate; paddle-wheel; 4-cyano-pyridine.

Abbreviations: CNpy, cyanopyridine, CSD, Cambridge Structural Database.

I. INTRODUCTION

A large part of coordination chemistry comprises of copper(II) complexes and they are very interesting owing to their wide range of applications [1-5]. A large number of dimeric paddle wheel type copper(II) carboxylate adducts, $[Cu_2(OOCR)_4L_2]$, have been reported where L is an apical ligand with a nitrogen atom. Research has been done on these type of complexes whether to clarify the factors influencing the intramolecular magnetic exchange interactions that occurs between the Cu(II) ions in a paddle-wheel unit or to investigate their catalytic properties etc [6, 7].

Copper(II) carboxylates with higher carboxylic acids e.g. those with longer alkyl groups, can exhibit thermotropic columnar mesophases and can be used as wood preservatives [8-10]. Kozlevčar *et al.,* had reported that dimeric complexes with the carboxylic (fatty) acids of different length are especially interesting owing to their biological activity as in preserving woods from the wood destroying fungi *Trametes versicolor* and *Antrodia vaillantii* [11]. Dinuclear copper(II) carboxylates because of their lower magnetic moments differ significantly from the other polymeric or monomeric Cu(II) complexes. They show antiferromgnetic coupling and indeed studies on the magnetic properties of such complexes as exemplified by “$Cu_2(\mu\text{–}O_2CCH_3)_4(H_2O)_2$’, copper(II) acetatate monohydrate, opened new vistas in the field of molecular magnetism [12].

Coordination compounds of long chain caprylato (octanoato) and caprato (decanoato) ligands were reported to show fungicidal activity [11]. Copper(II) caprylate complexes with nicotinamide and N,N-diethylnicotinamide as apical ligands and copper(II) caprylate and copper(II) caprates bearing pyridine ligands are known [11, 13]. A mononuclear copper(II) decanoate complex with ammonia and water as ligands was also reported [14]. Kozlevčar *et al.*, reported dimeric copper(II) decanoate with urea ligand [15]. However, dimeric caprylate complex of dimeric copper(II) containing substituted pyridine ligand like 4-cyanopyridine have not been reported yet as confirmed from searching in Cambridge Structural Database (CSD). Herein, we present the single crystal X-ray structure of dimeric paddle wheel copper(II) complex having long chain carboxylic acid and substituted pyridine ligand namely $[Cu_2(\mu\text{-}O_2CC_7H_{15})_4(4\text{-}CNpy)_2]$. The chemistry of the complex is discussed in some detail.

II. MATERIALS AND METHODS

The reagents and solvents used in this work were obtained from commercial sources and employed without further purification. The single crystal X-ray diffraction data of the complex were recorded using a Bruker Smart Apex II X-ray diffractometer.

A. Preparation of $[Cu_2(\mu\text{-}O_2CC_7H_{15})_4(4\text{-}CNpy)_2]$

$CuSO_4.5H_2O$ (0.749 g, 3m mol) was dissolved in methanol (25 ml). To this solution, sodium caprylate ($C_7H_{15}COONa$; 0.997 g, 6m mol) and 4-cyanopyridine (0.312 g, 3m mol) were added and the mixture was stirred for 2 h. The resulting green product was filtered off, washed with small volumes of methanol and dried in a vacuum desiccator over fused $CaCl_2$ (yield 82%). The product was dissolved in acetonitrile to get a greenish homogeneous solution which was allowed to concentrate by evaporation at room temperature. Single crystals suitable for X-ray diffraction was obtained from this solution after one day and collected by filtration.

(i) *X-ray Crystallographic Procedure*

The copper(II) complexes have been characterized by single crystal X-ray diffraction. Suitable crystals were picked up for X-ray crystallographic work by microscopic

examination. The structures were solved by direct methods (SHELXS-97) and standard Fourier techniques, refined on F^2 using full matrix least squares procedures (SHELXL-97) with SHELX-97 incorporated in WinGX [16, 17]. Structural illustrations were drawn using ORTEP-III for Windows and Mercury [18-20]. The non-hydrogen atoms were refined with anisotropic displacement parameters for all the structures.
Crystallographic and structure refinement details for the compound are listed in Table 1.

Table 1: Selected crystallographic data for [Cu_2(μ-$O_2CC_7H_{15}$)$_4$(4-CNpy)$_2$].

Details	**[Cu_2(μ-$O_2CC_7H_{15}$)$_4$(4-CNpy)$_2$]**
Crystal system, space group	Triclinic, $P\bar{1}$
Wavelength	0.71073 Å
Unit cell dimensions	a = 8.7834(4) Å, b = 9.7007(4) Å, c = 15.2529(7) Å α = 78.826 (3)≡, β = 87.470(3)≡, γ = 78.887(3)º
Volume	1224.72(9) Å^3
Z, Calculated density	3, 1.635 g/cm^3
Absorption coefficient	1.365 mm^{-1}
F(000)	624
Theta range for data collection	1.39 to 28.47º
Index ranges	-11<= h< 11, -11<=k<=12, -16<=k=20
Reflections collected / unique	15548 / 7940 [R(int) = 0.0825]
Program package	SHELX-97
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7940 / 3 / 528
GooF* on F^2	0.934
Final R indices [I>2□(I)]	R1 = 0.0621, wR2 = 0.1471
R indices (all data)	R1 = 0.0940, wR2 = 0.1600
(Shift / esd)$_{max}$	0.000

*GooF = $S = \{\Sigma[w(F_o^2-F_c^2)^2] / (n-p)\}^{½}$, $^\dagger wR2 = \{\Sigma[w(F_o^2-F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{½}$; $R1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$

III. RESULTS AND DISCUSSION

A. Crystal Structure of [Cu_2(μ-$O_2CC_7H_{15}$)$_4$(4-CNpy)$_2$]

The ORTEP view of complex as determined by single crystal X-ray diffraction technique is shown in Fig. 1. The molecular structure is shown to have structure similar to that of copper(II) acetate hydrate. The two Cu centres in [Cu_2(μ-$O_2CC_7H_{15}$)$_4$(4-CNpy)$_2$] are bridged by the four caprylato ligands with the two apical positions occupied by the two 4-cyanopyridine ligands being very similar to that observed in acetate and benzoate compounds [7, 21, 22]. The centre of symmetry is the midpoint of the Cu···Cu axis through which the two copper atoms are related. With fatty acid copper carboxylates, similar paddle wheel dimeric structures are rare and only structures with pyridine, Nicotinamide and N,N-diethylnicotinamide as apically positioned ligands have been reported. Cu–Cu distance of 2.6004(7) Å is shorter than the corresponding distance in [Cu_2(μ-O_2CCH_3)$_4$(H_2O)$_2$] (2.614 Å) as well as those in [Cu_2(μ-$O_2CC_7H_{15}$)$_4$(Et_2nia)$_2$] (2.6273 Å) and [Cu_2(μ-$O_2CC_7H_{15}$)$_4$(nia)$_2$] (2.6127 Å) but no bond is present between the two Cu atoms [23]. Equatorial Cu–O distances vary from 1.949(11) Å to 2.014(10) Å (Table 2) but axial Cu–N distance is longer which is 2.208(9) Å. The long Cu–L distance where L is an axial ligand is considered to be normal for [Cu_2(μ-O_2CR)$_4L_2$] type of structures [24]. In the dimer one pair of hydrocarbon chains has the common zigzag conformation while the other pair is distorted which probably facilitates efficient packing. From the O–Cu–O and O–Cu–N angles (Table 2), it can be seen that CuO_4N has distorted square pyramidal structure. The O–Cu–O has bond angle in the range 86.9(4)° to 167.7(4)° while O–Cu–N has in the range 91.0(4)° to 100.9(4)°. The Cu atom lies 0.1659 Å above the mean plane formed by the four basal O atoms towards the coordinated N atom.

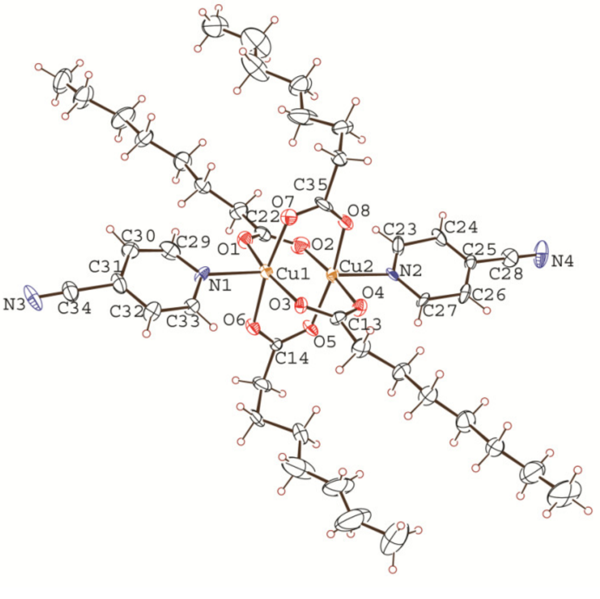

Fig. 1. ORTEP representation of complex [Cu_2(μ-$O_2CC_7H_{15}$)$_4$(4-CNpy)$_2$].

From the packing diagram it is evident that the crystal structure of [Cu_2(μ-$O_2CC_7H_{15}$)$_4$(4-CNpy)$_2$] is stabilized by C–H···O and C–H···N hydrogen bonds (Fig. 2). The hydrogen bridges result in the formation of a three dimensional supramolecular network. The observed H-bonding interactions are shown in Table 3.

Table 2: Selected bond lengths [Å] and angles [°] for [$Cu_2(\mu-O_2CC_7H_{15})_4(4-CNpy)_2$].

Distances/ Å			
Cu(1)-O(1)	1.949(11)	Cu(2)-O(2)	1.927(11)
Cu(1)-O(3)	2.001(8)	Cu(2)-O(4)	1.982(9)
Cu(1)-O(6)	2.014(10)	Cu (2)-O(5)	1.984(9)
Cu(1)-O(7)	1.951(10)	Cu(2)-O(8)	1.895(11)
Cu(1)-N(1)	2.208(9)	Cu(2)-N(2)	2.203(11)
Cu(1)-Cu(2)	2.6004(7)		

Angles/º			
O(1)-Cu(1)-O(3)	167.7(4)	O(2)-Cu(2)-O(4)	171.7(4)
O(1)-Cu(1)-O(6)	91.1(4)	O(2)-Cu(2)-O(5)	89.1(4)
O(1)-Cu(1)-O(7)	86.9(4)	O(2)-Cu(2)-O(8)	88.7(5)
O(3)-Cu(1)-O(6)	88.7(4)	O(4)-Cu(2)-O(5)	88.9(4)
O(3)-Cu(1)-O(7)	91.0(4)	O(4)-Cu(2)-O(8)	91.9(5)
O(6)-Cu(1)-O(7)	169.0(4)	O(5)-Cu(2)-O(8)	170.2(5)
O(1)-Cu(1)-N(1)	94.8(4)	O(2)-Cu(2)-N(2)	97.5(5)
O(3)-Cu(1)-N(1)	97.6(4)	O(4)-Cu(2)-N(2)	90.8(4)
O(6)-Cu(1)-N(1)	91.0(4)	O(5)-Cu(2)-N(2)	98.0(4)
O(7)-Cu(1)-N(1)	100.9(4)	O(8)-Cu(2)-N(2)	91.7(4)

Table 3: Geometric parameters of the hydrogen bonds in [$Cu_2(\mu-O_2CC_7H_{15})_4(4-CNpy)_2$].

Hydrogen bonds				
D–H···A	d(D–H)/Å	d(H···A)/Å	d(D···A)/Å	∠(DHA)/°
C(31)-H(31)...O(5)	0.93	2.580	3.175	122
C(36)-H(36B)...O(6)	0.97	2.774	3.593	142
C(7)-H(7B)...O(8)	0.97	2.857	3.674	142
C(6)-H(6B)...N(4)	0.97	2.765	3.627	149
C(37)-H(37B)...O(8)	0.97	2.808	3.631	143

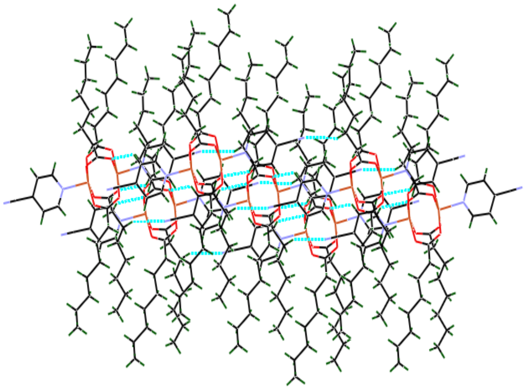

Fig. 2. Packing diagram of [$Cu_2(\mu-O_2CC_7H_{15})_4(4-CNpy)_2$] showing C–H···O and C–H···N interactions.

Our investigation has made it possible to develop a facile method to prepare dimeric copper(II) caprylate having paddle wheel geometry. A lot of dimeric paddle wheel copper(II) complexes have been reported till date [8, 25] but those with long chain carboxylate as ligand are only a few in number. In spite of the presence of long chain alkyl groups, it has been possible to determine the crystal structure satisfactorily. Petrič *et al.,* [14] reported a two step synthesis of dimeric Cu(II) caprylate complexes with pyridine ligand. However, our synthesis is quite a simple one step synthetic process for preparation of dimeric Cu(II) caprylate complex with substituted pyridine ligand. Further, the air stable product was also isolated in better yield compared to the previously reported method.

IV. CONCLUSION

We have presented the synthesis and characterization of a new dimeric long chain caprylato bridged copper(II) complexes displaying the paddle wheel geometry. Crystal data for the complex:Triclinic, $P\bar{1}$, a = 8.7834(4) Å, b = 9.7007(4) Å, c = 15.2529(7) Å, $\alpha = 78.826\ (3)^{\circ}$, $\beta = 87.470(3)^{\circ}$, $\gamma = 78.887(3)^{\circ}$, V = 1224.72(9) Å^3, D_c =1.635 g/cm^3 and Z = 3.

V. FUTURE SCOPE

Long chain alkyl groups in the carboxylato ligands imparts mesogenic characteristics to the copper(II) complex under study. This property could be exploited for further application such as in sensors. The synthesized long chain complex could also be studied for its microbial and fungicidal activity since the presence of bridging fatty acids along with apically positioned ligands are found to be bioactive [7, 8]. Thermal decomposition studies of the complex could also be carried out to analyze the nano morphology by varying reaction criteria under feasible conditions.

ACKNOWLEDGEMENT

I would like to thank the SAIF, Department of Instrumentation & USIC, Gauhati University, Guwahati, India, for the data collection. I would also like to thank UGC, India, for a scholarship awarded under its BSR Fellowship scheme.

Conflict of Interest. The authors declare no conflict of interest in this reported work.

REFERENCES

[1]. Mehrotra, R. C. and Bohra, R., (1983). Metal Carboxylates, Academic Press, London.

[2]. Premkumar, M., Kaleeswaran, D., Kaviyarasan, G., Prasanth, D. A. and Venkatachalam, G., (2019). Mono and Dinuclear Cu(II) Carboxylate Complexes with Pyridine and 1-methylimidazole as Co–Ligands: Synthesis, Structure, Antibacterial Activity and Catalytic Nitroaldol Reactions. *Chemistry Select*, *4*(25): 7507-7511.

[3]. Maqbool, S., Khan, M. U., Parvaiz, M. B. and Dwivedi, H. P., (2018). Synthesis, Characterization and Kinetic Studies of Quadri-dentate Demi-macrocyclic Complexes of Mn (II) and Cu (II) having di-aza and di-oxa Donor's. *International Journal of Theoretical & Applied Sciences, 10*(2): 33-39.

[4]. Qadir, A. M., Kansiz, S., Dege, N., Rosair, G. M. and Iskenderov, T. S., (2020). Crystal structure and Hirshfeld surface analysis of one-dimensional copper(II) coordination polymer incorporating succinate and tetra-methylethylenediamine ligands. *Acta Cryst*., *E76*: 1038-1041.

[5]. Politeo, N., Pisacic, M., Dakovic, M., Sokol, V. and Kukovec, B. M., (2020). The first coordination compound of deprotonated 2-bromonicotinic acid: crystal structure of a dinuclear paddle-wheel copper(II) complex. *Acta Cryst., E76*: 225-230

[6]. Doedens,R. J., (1976). Structure and Metal-Metal Interactions in Copper(II) Carboxylate Complexes. *Prog. Inorg. Chem., 21*: 209-229.

[7]. Sarmah, P., Das, B. K. and Phukan, P., (2010). Novel dicopper(II)-tetracarboxylates as catalysts for selective oxidation of benzyl alcohols with aqueous TBHP. *Catal. Commun., 11*(10): 932-935.

[8]. Burrows, H. D. and Ellis, H. A., (1982).The thermal behaviour and spectral properties of some long chain copper(II) carboxylates. *Thermochim. Acta., 52*(1-3): 121-129.

[9]. Abied,H., Guillon, D., Skoulios, A., Weber P., Giroud-Godquin, A. M. and Marchon, J. C., (1987). Investigation of the Structures of the Crystalline and Columnar Phases of Linear Chain Copper(II) Alkanoates. *Liq. Cryst.*, *2*(3): 269-279.

[10]. Kozlevčar, B., Lah,N., Leban, I., Turel, I., Šegedin, P., Petrič, M., Pohleven, F., White, A. J. P., Williams, D. J. and Giester, G., (1999). Fatty Acid Copper(II) Carboxylates with Nicotinamide - Characterization and Fungicidal Activity. Crystal Structures of Two Heptanoate Forms and Nonanoate. *Croat. Chem. Acta., 72*(2-3): 427-441.

[11]. Kozlevčar, B., Lah, N., Leban, I., Pohleven, F. and Šegedin, P., (2000). Synthesis and Characterization of Fatty Acid Copper(II) Carboxylates with N,N-Diethylnicotinamide. *Croat. Chem. Acta*, *73*(3): 733-741.

[12]. Kozlevčar, B., Radišek, M., Jagličic, Z., Merzel, F., Glažar, L. and Šegedin, P., (2007). Strong antiferromagnetism in the dinuclear 2-pyridone complex with N–C–O bridges: A *paddle-wheel* analogue of the dinuclear tetracarboxylates. *Polyhedron, 26*(18): 5414-5419.

[13]. Petrič, M., Leban, I. and Šegedin, P., (1995). Preparation and characterization of copper(II) coordination compounds with linear chain fatty acids with 7–12 carbon atoms and pyridine. Crystal structure of $Cu(O_2CC_8H_{17})_2(py)_2(H_2O)$. *Polyhedron, 14*(8): 983-989.

[14]. Petrič, M., Leban, I. and Šegedin, P., (1996).Complexes of copper(II) carboxylates with ammonia. Crystal structure of $Cu(O_2CC_9H_{19})_2(NH_3)_2(H_2O)$ *Polyhedron, 15*(23): 4277-4282.

[15]. Kozlevčar, B., Leban, I., Petrič, M.,Petriček S., Roubeau, O., Reedijk, J. and, Šegedin, P., (2004). Phase transitions and antiferromagnetism in copper(II) hexanoates: a new tetranuclear type of copper carboxylate *paddle-wheel* association. *Inorg. Chim. Acta, 357*(14): 4220-4230.

[16]. Sheldrick, G.M., SHELX-97, (1997). A Program for Crystal Structure Refinement of Crystal Structures; University of Göttingen : Germany.

[17]. Farrugia, L. J., (1999). WinGX suite for small-molecule single-crystal crystallography. *J. Appl. Cryst*., *32*: 837-838.

[18]. Burnett, M. N. and Johnson, C.K., (1996). ORTEP-III: Oak Ridge Thermal Ellipsoid Plot for Crystal Structure Illustrations Oak Ridge National Laboratory Report ORNL- 6895, U.S.

[19]. Farrugia, L. J., (1997). ORTEP-3 for Windows - a version of ORTEP III with a graphical user interface (GUI). *J. Appl. Cryst*., *30*: 565.

[20]. Mercury: Version 1.4.2, (2007) CCDC, Cambridge, UK.

[21]. Das, B. K., Bora,S. J. and Sarmah, P., (2007). Tetrakis(μ-benzoato-κ^{2}O:O′)bis(4-ethylpyridine-κN)-dicopper(II). *Acta Cryst.,E63*: m251-m252.

[22]. Bora, S. J., Sarmah, P., Phukan, P. and Das, B. K., (2007). Tetrakis (μ-benzoato-κ^2 O:O′)bis[4-(dimethylamino) pyridine-κN^1] dicopper(II). *Acta Cryst., C63*: m392-m394.

[23]. Brown, G. M. & Chidambaram, R., (1973). Dinuclear Copper(II) Acetate Monohydrate: a Redetermination of the Structure by Neutron-Diffraction Analysis. *Acta Cryst*., *B29*: 2393-2403.

[24]. Sundberg, M. R., Uggla, R. and Melnik, M., (1996). Comparison of the structural parameters in copper (II) acetate-type dimers containing distorted square pyramidal CuO_4O and CuO_4N chromophores. *Polyhedron*, *15* (7): 1157-1163.

[25]. Bette, S., Costes, A., Kremer, R. K., Eggert, G., Tang, C. C. and Dinnebier R. E., (2019). On Verdigris, Part III: Crystal Structure, Magnetic and Spectral Properties of Anhydrous Copper(II) Acetate, a Paddle Wheel Chain. *Z. Anorg. Allg. Chem*., *645*: 988–997.

How to cite this article: Baruah, S., Sarmah, N. and Das, B. K. (2020). Synthesis and Crystal Structure of [tetrakis (μ-caprylato)-bis-(4-cyanopyridine) copper(II)]. *International Journal on Emerging Technologies, 11*(5): 193–196.